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<b>(21) International Application Number:</b> PCT/IL98/00344 <b>(22) International Filing Date:</b> 24 July 1998 (24.07.98)  <b>(30) Priority Data:</b> 121402 27 July 1997 (27.07.97) IL 122115 5 November 1997 (05.11.97) IL  <b>(71) Applicant (for all designated States except US):</b> TECHNION RESEARCH AND DEVELOPMENT FOUNDATION LTD. [IL/IL]; Senate House, Technion City, Park Gootwirt, 32000 Haifa (IL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> EISEN, Moris, S. [IL/IL]; Hashkedim Street 68, 34601 Tyvon (IL). VOLKIS, Victoria [IL/IL]; Netive Hen Street 61/47, Neve-Sheanan, 32688 Haifa (IL). SHMULINSON, Michal [IL/IL]; Hschlav Street 9/1, Ramat Almogi, 34790 Haifa (IL). AVERBUJ, Claudia [IL/IL]; Einav Street 1/1, 21970 Karmiel (IL). TISH, Edith [IL/IL]; Arie Street 16/15, 78701 Ashkelon (IL).  <b>(74) Agent:</b> REINHOLD COHN AND PARTNERS; P.O. Box 4060, 61040 Tel-Aviv (IL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR THE PRODUCTION OF STEREOREGULAR POLYMERS AND ELASTOMERS OF $\alpha$ -OLEFINS AND CERTAIN NOVEL CATALYSTS THEREFOR		
<b>(57) Abstract</b> <p>The present invention provides a process for the pressure modulated polymerization of one or more <math>\alpha</math>-olefins having at least 3 carbon atoms, which comprises: contacting the monomer or monomers in a polar or non-polar solvent under polymerization conditions with a homogeneous catalyst system including: a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having C<sub>1</sub>, C<sub>2</sub>, or C<sub>3</sub> symmetry, provided that when a complex comprising only a single ligand is used for the production of stereoregular polystyrene, said single ligand has natural chirality, and b) an anion of a Lewis acid or a Brönsted acid; and adjusting the pressure so as to obtain at will either a highly stereoregular polymer or copolymer or an elastomer.</p>		

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**PROCESS FOR THE PRODUCTION OF STEREOREGULAR  
POLYMERS AND ELASTOMERS OF  $\alpha$ -OLEFINS AND  
CERTAIN NOVEL CATALYSTS THEREFOR**

**FIELD OF THE INVENTION**

The present invention relates to the use of octahedral transition metal complexes as precatalysts for the polymerization of  $\alpha$ -olefins, to homogeneous catalyst systems comprising these complexes and to a novel class of such  
5 complexes. More particularly, the invention relates to the use of cationic chiral, racemic or non chiral catalysts of the above mentioned type for the stereoregular polymerization of  $\alpha$ -olefins in order to produce highly stereoregular polymers or poly( $\alpha$ -olefin) elastomers.

**BACKGROUND OF THE INVENTION**

10 The polymerization of  $\alpha$ -olefins with the known Ziegler-Natta catalysts is well known in the chemical industry and used at a large extent. The various polymers that are derived from the polymerization of such olefins show differences in their chemical and physical properties, as a result of differences in molecular structure and molecular weights. Polymers of  $\alpha$ -olefins having 3 or  
15 more carbon atoms as the monomeric unit, will have pendant hydrocarbyl groups attached to the polymer backbone chain. The arrangement of these hydrocarbyl groups along the polymer backbone will determine, in major part, the physical properties of a particular polymer. For example, strong polymers tend to be

stereochemically regular, meaning that the adjacent hydrocarbyl groups reside on the same side of the polymer backbone.

Three major types of stereoregularity, or tacticity have been characterized and consist of atactic, isotactic and syndiotactic configurations. Atactic polyolefins are those wherein the pendant hydrocarbyl groups have no regular order in space with reference to the backbone. These are amorphous materials and are generally unsuitable for applications where high strength is required. Isotactic polyolefins are those wherein the pendant hydrocarbyl groups are ordered in space on the same side or plane of the polymer backbone chain. The degree of isotactic regularity may be measured by NMR techniques. Highly isotactic polyolefins exhibit a high degree of crystallinity and high melting points. Accordingly, isotactic polyolefins are adapted to high strength applications. Syndiotactic polyolefins are those wherein the pendant hydrocarbyl groups of the polymer backbone alternate sequentially from one side or plane to the opposite side or plane relative to the polymer backbone. Although syndiotactic polymers are characterized by lower melting points when compared to the corresponding isotactic polymers, they still are suitable for high strength applications, provided their molecular weight exceeds 100,000 daltons.

Polymers, which comprise alternating isotactic or syndiotactic (crystalline) and atactic (amorphous) stereosequences have elastomeric properties and are, therefore, called elastomers. Elastomer is a material which tends to regain its shape upon extension.

Conventional titanium and zirconium based Ziegler-Natta catalysts for the preparation of isotactic polymers are well known in the art. The systems are, however, limited in terms of molecular weight, molecular weight distribution and tacticity control. More recently, new methods of producing isotactic polymers from an alumoxane cocatalyzed metallocene were reported in Ewen J.A., J. Am. Chem. Soc., 106, 6355 (1984) and Kaminsky W. et al., Angew. Chem. Int. Ed. Eng., 24, 507 (1985).

The use of cocatalyzed catalyst systems for the production of highly crystalline polyolefins is disclosed in U.S. Pat. No. 5,318,935. The catalyst systems described therein comprise a complex formed upon admixture of the amido group IVb transition metal component with an alumoxane component.

5 According to a recent review (M. S. Eisen et al., J. Organometallic Chem., 503, 307 (1995)), a series of bis(trimethylsilyl)benzamidinate zirconium dichlorides are described as active catalysts for ethylene polymerization. As taught therein, the polymerization activity increases drastically with increase in pressure. However, these catalyst systems are generally characterized by a pronounced  
10 moisture-sensitivity due to the inherent hydrolytic instability imposed by the presence of several Si-N bonds in the molecules.

Homogeneous catalysts for stereoregular olefin polymerization are further disclosed in U.S. Pat. No. 5,330,948. According to this patent, by using a metallocene catalyst having a chiral substituent, selected from neomenthyl,  
15 menthyl and phenylmenthyl with a cocatalyst, a better control over the desired properties of the resulting polymer is achieved.

U.S. Pat. No. 5,594,080 describes metallocene catalysts bearing cyclopentadienyl-type ligands, which are used in the production of elastomeric polyolefins. The structure and therefore the properties of the obtained products  
20 depend on several factors, inter alia the olefin monomer pressure during the polymerization and the nature of the cyclopentadienyl-based ligands.

The synthesis of stereoregular polymers has been reported (M. Bochmann, J. Chem. Soc., Dalton Trans. 225, (1996); H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, Angew. Chem., Int. Ed. Engl. 34, 1143  
25 (1995)) by using chiral organo-group IV (Ti, Zr, Hf) catalysts having approximate  $C_2$  symmetry. Most of the ligands for these " $C_2$ " catalysts are based upon indenyl or related cyclopentadienyl components and are difficult and expensive to synthesize.

## OBJECTS OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method of  
5 polymerization of one or more  $\alpha$ -olefins to form polymers having a preselected range of properties, ranging from isotactic to elastomeric properties.

It is another object of the invention to provide improved, low-cost, homogeneous precatalysts for polymerization which, when used with an appropriate cocatalyst, permit the efficient polymerization of  $\alpha$ -olefins to produce  
10 stereoregular polymers.

It is another object of the invention to provide a new class of catalysts, which, as contrasted to the known catalysts that contain cyclopentadienyl ligands, are not decomposed when exposed to air or humidity.

## 15 SUMMARY OF THE INVENTION

The present invention thus provides a process for the pressure modulated polymerization of one or more  $\alpha$ -olefins having at least 3 carbon atoms, which comprises:

contacting the monomer or monomers in a polar or non-polar solvent under  
20 polymerization conditions with a homogeneous catalyst system including:

a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having  $C_1$ ,  $C_2$ , or  $C_3$  symmetry, provided that when a complex comprising only a single ligand is used for  
25 the production of stereoregular polystyrene, said single ligand has natural chirality, and

b) an anion of a Lewis acid or a Brönsted acid; and

adjusting the pressure so as to obtain at will either a highly stereoregular polymer or copolymer or an elastomer.

Further disclosed is a catalyst system for use in the above process, wherein each of the bidentate chelating ligands has natural chirality.

### BRIEF DESCRIPTION OF THE DRAWING:

In order to understand the invention, reference will be made by way of  
5 non-limiting example only, to the accompanying drawing, which illustrates schematically chiral octahedral transition metal complexes (Figures 1, 2, 3) comprising 1, 2 or 3 bidentate chelating ligands arrayed around the coordination sphere of the metal (M) and a mixture of racemic octahedral complexes (Figure 4).

### DETAILED DESCRIPTION OF THE INVENTION

10

As stated above, one object of the present invention is to provide a process for the pressure modulated polymerization of one or more  $\alpha$ -olefins having at least 3 carbon atoms, which comprises:

contacting the monomer or monomers in a polar or non-polar solvent under  
15 polymerization conditions with a homogeneous catalyst system including:

a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having C<sub>1</sub>, C<sub>2</sub>, or C<sub>3</sub> symmetry, provided that when a complex comprising only a single ligand is used for  
20 the production of stereoregular polystyrene, said single ligand has natural chirality, and

b) an anion of a Lewis acid or a Brönsted acid; and

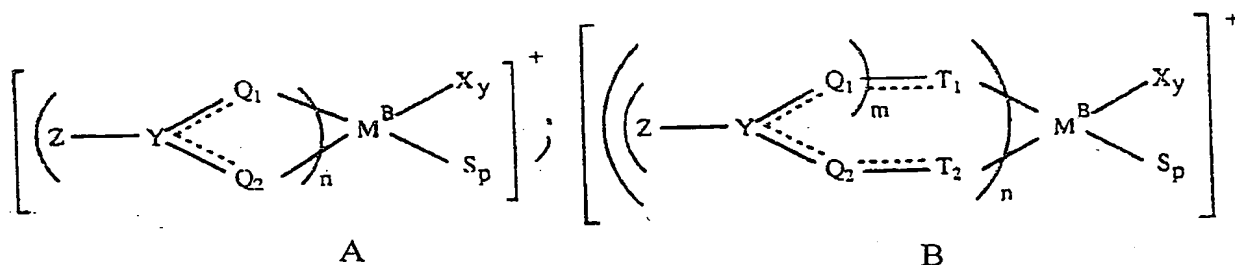
adjusting the pressure so as to obtain at will either a highly stereoregular polymer or copolymer or an elastomer.

25

A. The cationic form of the transition metal component

In a preferred embodiment, the cationic form of the transition metal component of the catalyst system is represented by formula A or B:

5



in which

- 15 M is a transition metal atom selected from groups 3,4,and 5 of the periodic table;  
 B is the valency of M and is 3, 4 or 5;  
 Y is C, N, S, P, B or Si;  
 Q<sub>1</sub> and Q<sub>2</sub> are the same or different and each is independently selected from O, OR,  
 N, NR, NR<sub>2</sub>, CR, CR<sub>2</sub>, S, SR, SiR<sub>2</sub>, B, BR, BR<sub>2</sub>, P, PR and PR<sub>2</sub>,  
 20 where each R can be the same or different and is independently H or a group  
 containing C, Si, N, O, B and/or P; and one or more R groups may be attached to M,  
 each replacing an X ligand;  
 Z is selected from H, OR, NR<sub>2</sub>, CR, CR<sub>2</sub>, CR<sub>3</sub>, SR, SiR<sub>3</sub>, PR<sub>2</sub> and BR<sub>2</sub>;  
 T<sub>1</sub> and T<sub>2</sub> are the same or different and each independently has the same meaning as  
 25 Q<sub>1</sub> and Q<sub>2</sub>;  
 X is an anionic ligand;  
 S is a solvent molecule;  
 m is 1,2 ,3 or 4;  
 n is 1, 2 or 3;



y is (B-n-1); and  
p is 0 or an integer to satisfy octahedral or capped octahedral coordination requirements of the transition metal; provided that when a complex comprising only a single ligand is used for the production of stereoregular polystyrene, said single  
5 ligand has natural chirality.

The transition metal M is preferably selected from Zr, Hf and Ti.

A particularly interesting class of complexes are those wherein Z and/or Q have natural chirality center(s), for example, menthyl, neomenthyl, myrtanyl and  $\alpha$ -phenethyl groups.

10 As can be seen in Figure 1 in the drawing, in case that  $n=1$ , the complex will have chirality (and thus, give rise to a racemic mixture of complexes) only when the single bidentate ligand includes a natural chiral center  $R^*$ . This requirement of chirality does apply only when highly stereoregular polymers are required and is not required when elastomeric polyolefins are the final product. Against this, the  
15 complexes depicted in Figures 2 and 3, wherein n is 2 or 3 respectively, exist as racemic mixtures (the enantiomeric pairs shown in the Figures), regardless whether or not the bidentate ligands include a natural chiral center. This is schematically shown for the case where  $n=2$  in Figure 4.

#### 20 B. Preparation of the complex

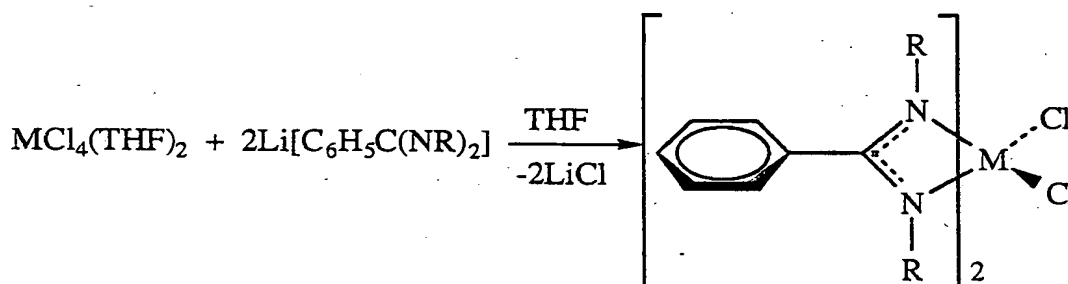
The complexes can be prepared by known methods, e.g. those described in J. Organometallic Chem. 503, 307 (1995) and in the references mentioned therein.

By way of example, the complex wherein the ligand comprises a chiral  
25 substituent  $R^*$  such as menthyl, myrtanyl or phenethyl, is obtained by reacting a chiral amine with a compound containing a group selected from alkyl, aryl and trimethylsilyl halide, in a high-boiling polar solvent such as tetrahydrofuran (THF). The resulting chiral amine compound, combined with an alkyl lithium complex and further with a nitrile group in a polar solvent selected from dimethoxyethane

(DME), dimethyl ether, dimethyl formamide or tetrahydrofuran, will produce a lithium salt. This salt may be either reacted with water to get the free ligand or reacted with a compound of the general formula  $MX'_4$ , wherein M is a cation derived from a transition metal, for example Ti, Zr or Hf, and X' is a halogen selected from Cl, Br or I ( $MX'_4$  preferably being  $ZrCl_4$ ) in a polar or non polar solvent. Examples of such solvents are diethyl ether, pentane, toluene, THF, DME, etc. The free ligand may be reacted with a compound of the general formula  $MX'_4$ , wherein M is a cation derived from a transition metal, for example Ti, Zr or Hf, and X' is a amido, phosphido, alkyl or aryl group ( $MX'_4$  preferably being  $Zr(N(CH_3)_2)_4$ ) in a polar or non polar solvent. Examples of such solvents are diethyl ether, pentane, toluene, THF, DME, etc.

According to one embodiment, the halogen may be replaced by various alkyl or phosphine groups.

A series of Ti and Zr complexes containing bulky benzamidinate ligands has been prepared, as shown in Scheme 1:



- 1: M = Ti, R = *i*-Pr
- 2: M = Zr, R = *i*-Pr
- 3: M = Ti, R = Cy
- 4: M = Zr, R = Cy

Scheme 1

$TiCl_4(THF)_2$  or  $ZrCl_4(THF)_2$  were reacted with two equivalents of  $Li[C_6H_5C(NC_3H_7)_2]$  or  $Li[C_6H_5C(NC_6H_{11})_2]$ , and afforded the bis-ligand complexes 1-4 in a crystalline form.

By analogy, the reaction of  $ZrCl_4$  with two equivalents of the substituted bis(trimethylsilyl)benzamidinate lithium-TMEDA complex (TMEDA-  $N,N,N',N'$ -

tetramethylethylenediamine) brought to the formation of the zirconium dichloride complexes in a crystalline form.

The cationic forms of the catalysts were generated by the reaction of the corresponding complexes with the cocatalyst.

5

### C. The cocatalyst

The catalyst system employed in the invention comprises a complex of the transition metal component and a cocatalyst in an excess ratio for aluminoxane cocatalysts and equimolar ratios for other Lewis acids or Brönsted acid cocatalysts.

10 Examples of suitable acids are oligomeric aluminoxanes and alkylaluminoxanes such as methylaluminoxane or perfluoroaromatic boron compounds such as  $B(C_6F_5)_3$ . Methyl aluminoxanes (MAO) having an average degree of oligomerization of from about 13 to about 25 are the most preferred.

15

### D. The polymerization process

The process comprises the steps of contacting an olefin monomer or mixture of monomers with the catalyst system in a suitable organic solvent and  
20 reacting the monomer(s) in the presence of the catalyst system under atmospheric pressure or elevated pressures, for a period and at a temperature sufficient to produce a polymer.

The polymerizations were carried out under rigorously anaerobic/ anhydrous vacuum line conditions, and reactions were quenched after appropriate  
25 times with methanol-HCl solutions prior to collection of the polymer, followed by washing with pentane and acetone and drying.

The monomer for the polymerization process is an  $\alpha$ -olefin having at least 3 carbon atoms, for example propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1,5-hexadiene, styrene or mixtures thereof.

According to the present invention, by modulating the pressure (monomer concentration in solution) of the polymerization reaction, the stereoregularity of the resulted products may be controlled, thus obtaining different products. Thus, for propylene for example, when an atmospheric pressure is employed, an atactic product will result having an oily or amorphous appearance. On the other hand, when a high pressure of above about two atmospheres is used, a highly stereoregular thermoplastic product is obtained, having more than 99% isotacticity and a melting point in the range of between 161-164°C. In a preferred embodiment, when the polymerization is carried out under a pressure alternating (in a controlled manner) between atmospheric and superatmospheric at a frequency lower than the polymerization insertion rate by a factor of from 1 to 100, then an elastomeric polyolefin is obtained.

#### E. Hydrogenation

15

The racemic mixture of C<sub>2</sub>-symmetry complexes or the monoheteroallylic complexes have been found to be also useful catalysts for the hydrogenation of olefins. Thus, in the presence of the catalysts of the present invention, ethane is formed from a mixture of ethylene and hydrogen. Since there is a competition between the insertion (polymerization) and the hydrogenation processes, the reaction can be driven towards the required product by controlling the partial pressure of the gases.

The present invention will be described in more detail with the aid of the following non-limiting examples.

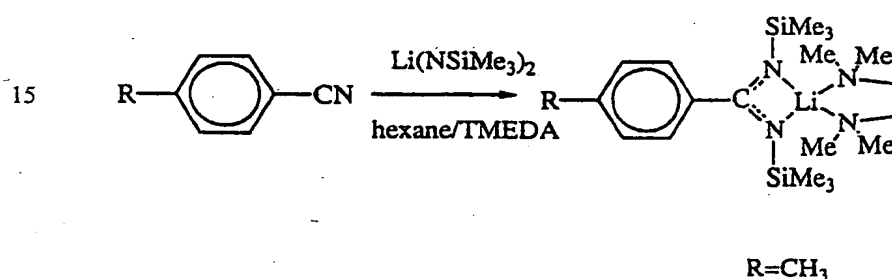
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All manipulation of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10<sup>-5</sup> torr) line, or in a nitrogen filled Vacuum Atmosphere glove box with a medium capacity

recirculator (1-2 ppm O<sub>2</sub>). Argon and nitrogen were purified by passage through a MnO oxygen-removal column. Ether solvents were distilled under argon from benzophenone ketyl. Hydrocarbon solvents (toluene-d<sub>8</sub>, C<sub>6</sub>D<sub>6</sub>, hexane) and TMEDA were distilled under nitrogen from Na/K alloy. All solvents for vacuum  
 5 line manipulations were stored under vacuum over Na/K alloy in resealable bulbs. Nitrile compounds (Aldrich) were degassed and freshly distilled under argon.

LiN(TMS)<sub>2</sub>, 4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-(NSiMe<sub>3</sub>)<sub>2</sub>Li•TMEDA, C<sub>6</sub>H<sub>5</sub>C[NC(i-Pr)<sub>2</sub>]<sub>2</sub>Li and C<sub>6</sub>H<sub>5</sub>C[NC(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sub>2</sub>Li•TMEDA were prepared according to methods known in  
 10 the art.

**EXAMPLE 1. Synthesis of 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C(NSiMe<sub>3</sub>)<sub>2</sub>Li-TMEDA**



20 **Scheme 2**

15.86g (0.095 mol) of LiN(trimethylsilyl)<sub>2</sub> were stirred in a hexane suspension (180 ml) at 0°C and then 11.1 g (0.095 mol) of 4-methylbenzonitrile were slowly added. The temperature of the mixture was  
 25 slowly raised to about 50°C and stirred for three additional hours.

After cooling to room temperature, an amount of 14.48 g (0.123 mol) of TMEDA were added and the solution stirred for about one hour. During the addition of the TMEDA, the color of the solution turned to brown-red and after several minutes, a large amount of the above product precipitated. The

solution stood overnight at about  $-50^{\circ}\text{C}$  and was filtered while cold. The precipitate was dried under a high vacuum, obtaining 31.6 g of a white crystalline product (yield 83%).

5     **Example 2. Synthesis of dichloro-bis(N,N'-trimethylsilyl-4-methylbenzamidinato)-zirconium(IV).**

To a solution of 5.96 g (15.8 mmol) of  $\text{ZrCl}_4(\text{THF})_2$  in 130 ml of THF, a solution of 12.66 g (31.6 mmol) of  $\text{Li}[4\text{-CH}_3\text{C}_6\text{H}_5\text{C}(\text{NSi}((\text{CH}_3)_3)_2)]$  in 100 ml of THF was added while stirring. The reaction mixture was stirred overnight at  
10 room temperature and the solvent was removed under vacuum. The residue obtained was extracted with 80 ml of toluene and the precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 20 – 30 ml of hexane and dried under vacuum for about 12 hours, obtaining 19.49 g of a yellow product (the yield  
15 being 86%).

**Example 3. Synthesis of dichloro-bis(N,N'-dicyclohexylbenzamidinato)-titanium(IV).**

20

To a solution of 5.27 g (15.8 mmol) of  $\text{TiCl}_4(\text{THF})_2$  in 130 ml of THF, a solution of 9.97 g (34.3 mmol) of  $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_{11})_2]$  in 100 ml of THF was added while stirring. The reaction mixture was stirred overnight at room temperature and the solvent was removed under vacuum. The residue obtained  
25 was extracted with 80 ml of toluene and the precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 20 – 30 mls of hexane and dried under vacuum for about 12 hours, obtaining 9.2 g of a red product (the yield being 80.5%).

**EXAMPLE 4. Synthesis of dichloro-bis(N,N'-diisopropylbenzamidinato)-zirconium(IV).**

5 To a solution of 7.54 g (20.0 mmol)  $\text{ZrCl}_4(\text{THF})_2$  in 130 ml THF, a solution of 8.41 g (40.0mmol) of  $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_3\text{H}_7)_2]$  in 100 ml of THF, was added dropwise at room temperature over a period of 15 minutes. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the residue extracted with 80 ml of toluene. The  
10 precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with hexane (20-30 ml) and dried under vacuum, for about 12 hours, thus obtaining 6.78g (60%) of a pale yellow, crystalline powder.

15 **EXAMPLE 5. Synthesis of dichloro-bis(N,N'-dicyclohexyl-benzamidinato) zirconium(IV)**

To a solution of 5.96g (15.8 mmol)  $\text{ZrCl}_4(\text{THF})_2$  in 130 ml THF, a solution of 9.97 g (34.3 mmol)  $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_{11})_2]$  in 100 ml THF was added  
20 dropwise. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuum and the residue extracted with 80 ml of toluene. The precipitated LiCl was filtered through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with hexane (20-30 ml) and dried under vacuum, for about 12 hours, thus obtaining 9.02 g (75%) of a red  
25 product.

**EXAMPLE 6. Synthesis of dichloro-bis(N,N'-diphenylbenzamido)-zirconium (IV).**

To a solution of 6.49 g (17.2 mmol)  $\text{ZrCl}_4(\text{THF})_2$  in 130 ml THF, a  
5 solution of 9.53 g (34.3mmol)  $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)_2]$  in 100 ml THF was added  
dropwise. The reaction mixture was stirred overnight at room temperature.  
The solvent was removed in vacuum and the residue extracted with 80 ml of  
toluene. The precipitated LiCl was filtered through a thin layer of Celite  
filter-aid. The clear filtrate was evaporated to dryness, washed with hexane  
10 (20-30 ml) and dried under vacuum for about 12 hours, thus obtaining 8.82 g  
(79%) of a pale yellow product.

**Example 7: Polymerization of an olefin**

An amount of 6 mg ( $8.7 \times 10^{-3}$  mmol) of the catalyst as described in  
15 Example 3 and 200 mg of MAO were introduced into the reactor, pumped-down  
and back-filled three times. The flask was reevacuated and 30 ml of toluene  
(dried over Na/K), or  $\text{CH}_2\text{Cl}_2$  (dried over  $\text{CaH}_2$ ), were transferred by vacuum  
into the reactor.

Large excess gaseous propylene was introduced into the reactor at  $-78^\circ\text{C}$   
20 through a gas purification column. The reactor was heated to the required  
temperature and the gas pressure was obtained from the well known  
pressure:temperature relationships. A rapid stirring of the solution was started  
after temperature equilibration and after a period of about two hours, the  
polymerization was quenched by injecting a mixture of methanol/HCl.

25 The polymeric product was filtered, washed with acetone and pentane  
and dried under vacuum. The methanol- insoluble fraction (more than 98% of  
the product) was extremely high crystalline, being 98.5% isotactic as measured  
by  $^{13}\text{C}$  NMR spectroscopy and had a DSC melting point of between  $156^\circ\text{C}$  and  
 $165^\circ\text{C}$ .



**Example 8: Olefin copolymerization**

An amount of 6 mg ( $8.7 \times 10^{-3}$  mmol) of the catalyst of Ex.5 and 200  
5 mg of methylalumoxane (MAO) were introduced into the reactor and connected  
to a high vacuum line. The reactor vessel was pumped-down and back filled  
three times, the flask was evacuated and an amount of 30 ml of toluene (dried  
over Na/K) was transferred by vacuum into the reactor.

A large excess mixture of gaseous propylene and butene (50%/50%) were  
10 introduced into the reactor, through the gas purification column. The reactor  
was heated to the requested temperature for which a given pressure is obtained.  
After temperature equilibration rapid stirring of the solution was initiated and  
after about 2 hours, the resulted polymer was quenched by injecting a mixture of  
methanol/HCl, thus producing a copolymer of isotactic polypropylene-  
15 butylene.

The above polymeric product was collected by filtration, washed with  
acetone and pentane and dried under vacuum. The methane-insoluble fraction  
(amounting to above 90% of the product) was extremely high crystalline, being  
between 98% to 99% isotactic as determined by  $^{13}\text{C}$  NMR spectroscopy.

20 In a similar manner, a block copolymerization can be obtained by  
reacting first 100% of propylene and then carrying out the reaction under an  
atmosphere of 100% butene and finally quenching the resulted product.

**Example 9: Olefin hydrogenation**

25

An amount of 6 mg ( $8.7 \times 10^{-3}$  mmol) of the catalyst of Example 4 and 200  
mg of MAO were introduced into a reactor containing a magnetic stirring bar.  
The reactor was connected to a high vacuum line, pumped-down and back-filled  
three times, the vessel reevacuated and an amount of 30 ml of toluene (dried

over Na/K) or pentane was added by vacuum therein. A mixture of gaseous propylene and hydrogen gas (50%/50%) was introduced into the reactor, through a gas purification column. The hydrogenation started almost immediately and could be monitored manometrically to completion.

5

**EXAMPLE 10: Preparation of a rubbery polymer**

An amount of 6 mg ( $8.7 \times 10^{-3}$  mmol) of the catalyst of Example 2 and 200 mg of MAO were charged in the reactor connected to a high vacuum line, pumped down and back-filled three times, the flask reevacuated and 30 ml of  
10 toluene (dried over Na/K) or  $\text{CH}_2\text{Cl}_2$  (dried over  $\text{CaH}_2$ ) were vacuum transferred into the reactor. Propylene was introduced into the reactor, the temperature being equilibrated to about  $50^\circ\text{C}$ . The pressure of the vessel was monitored to 10 atmospheres and the polymerization started immediately.  
15 Afterwards, the pressure was reduced by means of a piston to atmospheric pressure and back to high pressure with a frequency lower than the polymerization insertion rate of the isotactic reaction by a factor of from 1 to 100.

An atactic polymer was obtained at atmospheric pressure, while an  
20 stereoregular polymer was obtained at a high pressure. In this manner, by maintaining the frequency pressure change, a rubbery polymer is obtained, containing in each individual chain, both types of isotactic and atactic fragments.

Thus, by using this method, we prepared elastomeric poly-propylene, polybutene, polyhexene and others.

25

**EXAMPLE 11: Preparation of rubbery co-homopolymer**

In a similar manner, block copolymerization can be obtained by first reacting 100% propylene at a high pressure and then reacting the same

propylene under an atmospheric pressure.

**EXAMPLE 12: Preparation of a rubbery co-heteropolymer**

5       The process of Example 10 was repeated, wherein first the propylene was polymerized at a high pressure and then butylene was reacted at an atmospheric pressure, thus producing a rubbery heteropolymer.

**EXAMPLE 13. Preparation of a rubbery co-heteropolymer**

10       The procedure of Example 10 was repeated using a mixture of propylene and styrene as monomers and the polymerization was carried out in a reactor under normal pressure. A rubbery co-heteropolymer having sequences of atactic polypropylene and syndiotactic polystyrene was obtained.

15       **EXAMPLE 14. Preparation of a rubbery homopolymer with a non chiral non racemic complex.**

20       An amount of 10 mg (0.0198 mmol ) of the catalyst (4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)-C{N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>}TiCl<sub>3</sub>·THF and 300 mg of MAO were charged in the reactor connected to a high vacuum line, pumped down and back-filled three times, the flask reevacuated and 5 ml of toluene (dried over Na/K) or CH<sub>2</sub>Cl<sub>2</sub> (dried over CaH<sub>2</sub>) were vacuum transferred into the reactor. Propylene was introduced into the reactor, the temperature being equilibrated to about 50°C. The pressure of  
25 the vessel was monitored to 10.2 atmospheres and the polymerization started immediately.

0.9 g of an elastomeric polypropylene was obtained and characterized by <sup>13</sup>C-NMR spectroscopy .

**Example 15: Synthesis of  $[(\text{Me}_3\text{SiNCH})_2\text{CH}]\text{Zr}(\text{NMe}_2)_2$**

To a solution of 4.27 g (16 mmol) of  $\text{Zr}(\text{NMe}_2)_4$  in 130 ml of THF, a solution of 6.84g (32.0 mmol) of  $(\text{Me}_3\text{SiNCH})_2\text{CH}$  in 150 ml of THF was added while stirring at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature, then heated under reflux for 16 hours and the solvent was removed under vacuum. The residue obtained was recrystallized from a mixture of toluene:hexane (20:80%) to obtain 6.19 g of a yellow product (the yield being 64%).

**Example 16. Polymerization of propylene using  $[(\text{Me}_3\text{SiNCH})_2\text{CH}]\text{Zr}(\text{NMe}_2)_2$**

A heavy wall glass reactor was charged into a glovebox with 10 mg of  $(\text{Me}_3\text{SiNCH})_2\text{CH}]\text{Zr}(\text{NMe}_2)_2$  and 800 mg of MAO, removed from the glovebox and connected to a high vacuum line. 20 ml of toluene was vacuum transferred to the reactor and 25 ml of liquid propylene were transferred to the reactor. After temperature equilibration to room temperature a rapid stirring of the solution was started and after a period of two hours the polymerization was quenched. The polymeric product was filtered and washed to obtain a high crystalline polypropylene (mmmm 98.5%) with a mp of  $152^\circ\text{C}$ .

**CLAIMS:**

1. A process for the pressure modulated polymerization of one or more  $\alpha$ -olefins having at least 3 carbon atoms, which comprises:

contacting the monomer or monomers in a polar or non-polar solvent under  
5 polymerization conditions with a homogeneous catalyst system including:

a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having  $C_1$ ,  $C_2$ , or  $C_3$  symmetry, provided that when a complex comprising only a single ligand is used for  
10 the production of stereoregular polystyrene, said single ligand has natural chirality, and

b) an anion of a Lewis acid or a Brönsted acid; and

adjusting the pressure so as to obtain at will either a highly stereoregular polymer or copolymer or an elastomer.

15

2. A process according to claim 1, wherein said anion is derived from a cocatalyst.

3. A process according to claim 2, wherein said cocatalyst is selected from aluminoxane, methylaluminoxane or  $B(C_6F_5)_3$ .

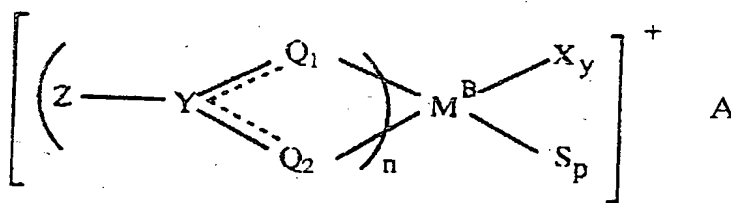
20

4. A process according to any one of claims 1 to 3, wherein said transition metal is selected from metals of groups 3, 4 and 5 of the periodic table.

25

5. A process according to any one of claims 1 to 4, wherein said transition metal is selected from Zr, Hf or Ti.

6. A process according to any one of the preceding claims wherein the  $\alpha$ -olefin is selected from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, styrene or mixtures thereof.
7. A process according to any one of claims 1 to 6 wherein the  $\alpha$ -olefin is propylene.
8. A process according to any one of the preceding claims wherein the  $\alpha$ -olefin is a mixture of propylene and styrene.
9. A process according to claim 1, wherein the cationic form of said transition metal component of the complex has the formula A:



in which

M is a transition metal atom selected from groups 3,4, and 5 of the periodic table;

B is the valency of M and is 3, 4 or 5;

Y is C, N, S, P, B or Si;

$Q_1$  and  $Q_2$  are the same or different and each is independently selected from O, OR, N, NR, NR<sub>2</sub>, CR, CR<sub>2</sub>, S, SR, SiR<sub>2</sub>, B, BR, BR<sub>2</sub>, P, PR and PR<sub>2</sub>,

where each R can be the same or different and is independently H or a group containing C, Si, N, O, B and/or P; and one or more R groups may be attached to M,

each replacing an X ligand;

Z is selected from H, OR, NR<sub>2</sub>, CR, CR<sub>2</sub>, CR<sub>3</sub>, SR, SiR<sub>3</sub>, PR<sub>2</sub> and BR<sub>2</sub>;

X is an anionic ligand;

S is a solvent molecule;

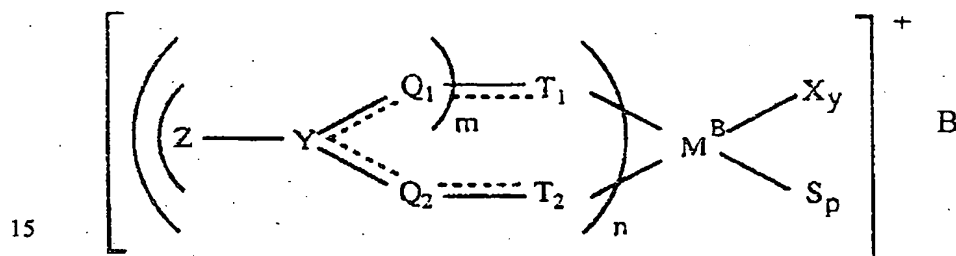
n is 1, 2 or 3;

y is (B-n-1); and

p is 0 or an integer to satisfy octahedral or capped octahedral coordination requirements of the transition metal; provided that when a complex comprising only a single ligand is used for the production of stereoregular polystyrene, said single  
5 ligand has natural chirality.

10. A process according to claim 1, wherein the cationic form of said transition metal component of the complex has the formula B:

10



in which M, B, Y, Q<sub>1</sub>, Q<sub>2</sub>, Z, X, S, n, y and p are as defined in claim 9;

T<sub>1</sub> and T<sub>2</sub> are the same or different and each independently has the same meaning as Q<sub>1</sub> and Q<sub>2</sub> in claim 9, and

20 m is 1, 2 or 3; provided that when a complex comprising only a single ligand is used for the production of stereoregular polystyrene, said single ligand has natural chirality.

11. A process according to claim 9 or 10, wherein M is selected from Zr, Hf, or  
25 Ti.

12. A process according to any one of claims 9 to 12, wherein n is 1 and at least one of Z and R has natural chirality.

13. A process according to claim 12, wherein Z and/or R is/are selected from menthyl, neomenthyl, myrtanyl,  $\alpha$ -phenetyl.
14. A process according to any one of the preceding claims wherein the  
5 polymerization is carried out under superatmospheric pressure of above 2 atmospheres, to obtain a highly stereoregular polyolefin.
15. A process according to any one of claims 1 to 13, wherein the  
10 polymerization is carried out under superatmospheric pressure of above 2 atmospheres, to obtain an elastomeric polyolefin.
16. A process according to any one of claims 1 to 13, wherein the  
polymerization is carried out under a pressure alternating between atmospheric  
and superatmospheric, at a frequency lower than the polymerization insertion rate  
15 by a factor of from 1 to 100, to obtain an elastomeric polyolefin.
17. A process according to any one of claims 1 to 13, wherein the  
polymerization is carried out with a catalyst where  $n=1$  to obtain an elastomeric  
polyolefin.  
20
18. A catalyst system as defined in claim 1, wherein each of said bidentate  
chelating ligands has natural chirality.



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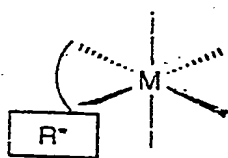


FIG A1

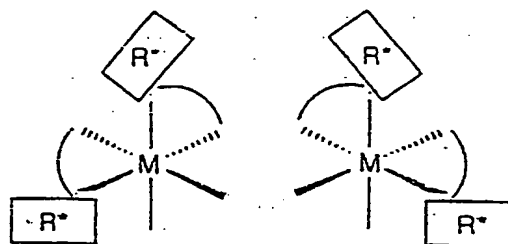


FIG A2

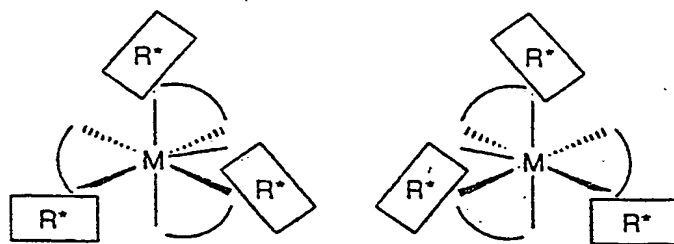


FIG A3

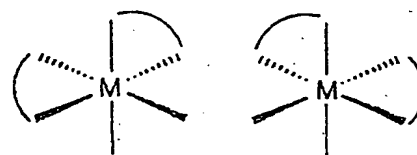


FIG B

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP98/00344

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08F10/00 C08F4/602

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 675 138 A (IDEMITSU KOSAN CO) 4 October 1995  see claims; page 10, lines 1-2; page 14, example 9	1-9, 11-15, 17, 18
X	EP 0 687 693 A (BASF AG) 20 December 1995  see claims; page 6, lines 24-27 and 34-36  -/-	1-9, 11-15, 17, 18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 October 1998

Date of mailing of the international search report

04/11/1998

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/ISA/8/00344

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	<p>FLORES J C ET AL:  "N,N'-BIS(TRIMETHYLSILYL)BENZAMIDINATOTITANIUM AND -ZIRCONIUM COMPOUNDS, SYNTHESIS AND APPLICATION AD PRECURSORS FOR THE SYNDIOSPECIFIC POLYMERIZATION OF STYRENE" ORGANOMETALLICS,  vol. 14, no. 4, April 1995, pages 1827-1833, XP000606086  see page 1827, abstract; page 1828, left-hand column, lines 6-18; page 1830, left-hand column, lines 1-13</p> <p>---</p>	1-9, 11-13, 17,18
X	<p>WALTHER D ET AL: "Zirkoniumorganische Chemie mit anorganischen Donorliganden N,N'-Bis(trimethylsilyl)benzamidinat (Siam) in Verbindungen des Typs (Siam)<sub>2</sub>ZrX<sub>2</sub> (X=Methyl, Benzyl, Allyl, Chlorid, oder Iodid) und (Siam)<sub>3</sub>ZrX (X=Chlorid)"  JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 508, no. 1, 8 February 1996, page 13-22 XP004036201  see page 13, abstract; page 21, paragraph 6.8.2.</p> <p>---</p>	1-9, 11-13, 17,18
X	<p>SCOLLARD J D ET AL: "POLYMERIZATION OF ALPHA-OLEFINS BY CHELATING DIAMIDE COMPLEXES OF TITANIUM" MACROMOLECULES,  vol. 29, no. 15, 15 July 1996, pages 5241-5243, XP000596747  see page 5241, right-hand column, scheme 1; page 5242, left-hand column, last paragraph</p> <p>---</p>	1-13,17, 18
X	<p>US 5 318 935 A (CANICH JO ANN M ET AL)  7 June 1994  cited in the application  see claims; column 6, lines 7-12; column 7, line 60 to column 8, line 2; column 9, line 55 to column 10, line 9</p> <p>---</p>	1-15,17, 18
E	<p>WO 98 34961 A (IMUTA JUNICHI; SAITO JUNJI (JP); FUJITA TERUNORI (JP); SUGIMURA KE)  13 August 1998  see pages 57-62</p> <p>---</p> <p style="text-align: center;">-/--</p>	1-18

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB/98/00344

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HERSKOVICS-KORINE D ET AL:            "Bis(trimethylsilyl)benzamidinate            zirconium dichlorides. Active catalysts            for ethylene polymerization"            JOURNAL OF ORGANOMETALLIC CHEMISTRY,            vol. 503, no. 2, 15 November 1995, page            307-314 XP004023639            cited in the application            see page 307, abstract; page 307,            left-hand column, lines 8-12; page 310,            left-hand column, lines 23-27            -----</p>	1-18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IL98/00344

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EP 0675138	A	04-10-1995	JP 7002917 A	06-01-1995
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WO 9834961	A	13-08-1998	NONE	

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